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Transport of urban-derived organic contaminants into a boreal lake: a case study with passive samplers

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The aim of this study was to evaluate the sources, transport and distribution of hydrophobic organic contaminants produced in an urban area. Passive sampling devices (PSDs) were employed in the storm-water drainage of the city of Lahti, in an adjacent boreal lake (Vesijärvi) and along its shore. Samples were analysed for 16 polycyclic aromatic hydrocarbons (PAHs) and 28 polychlorinated biphenyls (PCBs) with a gas chromatograph–mass spectrometer. Concentrations of contaminants were elevated in the stormwater drainage and in the vicinity of the stormwater outlets in Vesijärvi, but declined as a function of distance from the shore. Atmospheric PAH concentrations were significantly higher in the autumn than in the summer. Petrogenic PAHs contributed significantly to stormwater contamination, while pyrogenic pollutants mainly appeared to be carried to Vesijärvi by atmospheric transport.

Introduction

It is well known that presence of hydrophobic organic contaminants poses great risks for aquatic ecosystems. Some of these contaminants are ubiquitous in the environment, but large amounts often originate from anthropogenic activity, which is concentrated in urban areas. Many organic micropollutants are known to be produce and spread in urban areas. In many countries, including Finland, cleaning of urban stormwater is not required and it is directly discharged into adjacent waterbodies.

The city of Lahti is a growing Finnish urban area with approximately 100 000 inhabitants. It has a developed traffic system, several power plants burning coal, and approximately 100-year-long history of industrialization. Factories producing plywood, cardboard, yeast and furniture, as well as sawmills and smelters all functioned in the Lahti urban area during the last century. Vesijärvi — a lake whose surface area is 109 km^2 — receives untreated surface runoff from the city. Recent research has demonstrated that notable concentrations of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are present in the sediments of the lake. They were also found to be elevated in the vicinity of drainage outlets (Eronen 2008, Honkonen and Rantalainen 2013). PAHs in the lake sediments were determined to be of pyrogenic origin (gasoline, diesel and coal combustion). At the same time, sediments from stormwater traps in Lahti were found to predominantly contain asphalt-derived contaminants (Honkonen and Rantalainen 2013).

PAHs and PCBs are amongst the most frequently detected urban-derived contaminants.

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PAHs are widespread in the environment and often originate from anthropogenic sources, such as fossil-fuel combustion or direct release of petroleum products. PCBs are not ubiquitous in the environment, but still occur due to their extensive application in the past and long-range transport. Both PAHs and PCBs can be toxic to aquatic life and are recognized as priority pollutants of stormwater (Eriksson *et al*. 2005, 2007a, 2007b). Hydrophobic compounds such as PAHs and PCBs are easily sorbed to particulate matter and tend to accumulate in sediments, but they are also present in dissolved and colloidal forms. Dissolved chemicals are more readily bioavailable, which increases their relative importance to ecosystem health. Therefore, we considered it important to examine the fate of urban-derived organic contaminants in both lake water and urban air.

Semipermeable membrane devices (SPMDs) are frequently used for monitoring hydrophobic pollutants in water and air. They accumulate contaminants by passive diffusion across a polyethylene membrane into the lipid. This process resembles bioaccumulation and allows the bioavailable concentrations of lipophilic pollutants to be determined (Huckins *et al*. 1993). Passive sampling devices are especially useful when the investigated chemicals are present at trace levels and are not easily detectable by conventional sampling methods. SPMDs are usually exposed to contaminated media for an extended period of time (approx. 3–4 weeks). The mass of a pollutant accumulated by a sampler should reflect the time-averaged concentration to which sampler was exposed (Vrana *et al*. 2005). Sampling rates (R_s, l day^{-1}) for numerous hydrophobic substances, including PAHs and PCBs, can be found from previous studies on both water and air (Meadows *et al*. 1998, Huckins *et al*. 1999, Cranor *et al*. 2009). Furthermore, the operational costs and effort required for passive sampling are considerably lower as compared with those of conventional grab sampling of the same water and/or air volumes. Therefore, we considered passive sampling to be a reasonable choice for this research.

In our study, SPMD-like PSDs were employed across an expected contamination gradient in Vesijärvi, in the Lahti stormwater drainage system and in the urban atmosphere. The purpose of this research was to evaluate the distribution of dissolved PAHs and PCBs in the Lahti urban area, follow their transport to the aquatic ecosystem, and investigate the prevalent sources of pollution. The results of this study may help to clarify the main origins, emission pathways and distribution of urban-derived organic pollutants the Vesijärvi water column.

Material and methods

HPLC-grade hexane was purchased from Merck (Darmstadt, Germany) concentrated (95%–98%) sulphuric acid from Avantor Performance Materials (Center Valley, Pennsylvania, USA), triolein lipid (99%) from Sigma-Aldrich (St. Louis, Missouri, USA), and LDPE layflat tubing (width 2.5 cm, wall thickness 72 ± 1.7 μm) from Cope Plastics Inc. (Alton, Illinois, USA). A deuterated PAH mixture (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12), a solution of the 16 EPA PAHs and a recovery standard, anthracene-d10, were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany). A ^{13}C-labelled PCB internal standard solution mixture (PCB-52L, PCB-101L, PCB-138L and PCB-178L) was purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada), and a solution of 28 PCB congeners and the recovery standard PCB-204 from Accustandard Inc. (New Haven, Connecticut, USA).

PSDs in two different sizes were prepared from low-density polyethylene (LDPE) layflat tubing, cut into lengths of 48 (15) cm and cleaned by soaking overnight in hexane. One end of the tubing was sealed with a heat sealer and 0.4 (0.2) ml of triolein was placed inside as a thin layer. After that, 150 (50) ng of the performance reference compound (PCB-30) was added to the tube and the other end was sealed. The final length of the lipid-filled part was 43 (10.0) cm, and the mass of the sampler was 2.3 (0.7) g. Ready PSDs were stored at –20 °C, and transported to the sampling site and back in screw-top glass bottles.

Sample collection

In June 2010, passive sampling of water was per-

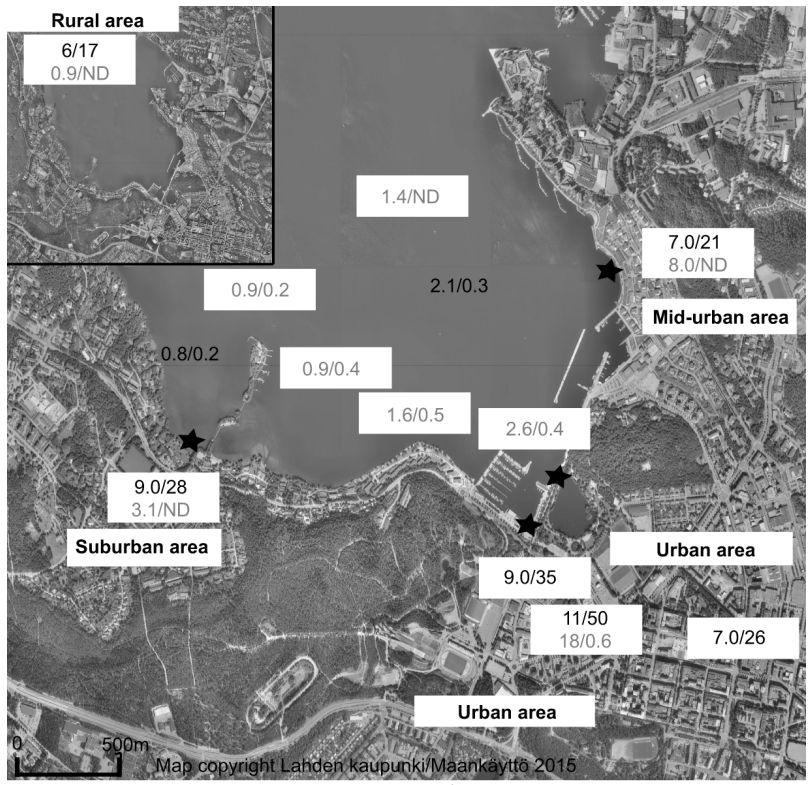

Fig. 1. PAH and PCB distributions in the Vesijärvi water column, stormwater and air of the Lahti urban area.

formed in Vesijärvi and in the Lahti stormwater drainage system. During the summer, the ambient water and air temperatures in the area are closest to the standard conditions (18 °C for water; 22 °C for the air) used for sampling rate (R_s) determination (Huckins *et al*. 1999, Cranor *et al*. 2009). The amount of stormwater runoff in the summer months is usually moderate, which makes the determination of average pollutant concentrations over a longer period more reliable. Eight sampling sites representing different degrees of urbanization of the adjacent shore were selected in Vesijärvi (Fig. 1). Larger PSDs were placed in metallic cages (three samplers per site) and fixed at a depth of about 1 m below the water surface for 26 days. Concentrations of organic pollutants in the liquid phase of urban runoff were monitored with mini-PSDs at three locations (urban, mid-urban, suburban). Water samples (8 l each) were taken from drainage wells three times a week and transferred to metal containers. A control PSD was exposed to tap water and treated similarly to the others. During the 21-day exposure, two mini-PSD samplers were placed in each container. Water was continuously circulated by an aquarium pump and replaced three times a week with a fresh sample. Twenty-four PSD samplers were employed during two air-sampling campaigns in June (non-heating season) and October (heating season) 2010. Six sampling sites, including a rural control, were chosen to represent different degrees of urbanization. Two parallel samplers per site were used. The samplers were placed in metallic containers, the open side facing downwards, and the exposure lasted for 25 days in June and 29 days in October. After exposure, the samplers were removed from the water or air, wiped and rinsed with ethanol, placed into glass bottles and stored at –20 °C prior to analysis.

Sample preparation and analysis

For dialysis, one side of the sampler was cut

open and internal standards (400 ng of each deuterated PAH and 20 ng of ^{13}C-labelled PCBs) were added to each sample, including a blank sampler and a field blank. Organic pollutants were then extracted by dialysis in 50 ml of *n*-hexane for 48 h with solvent exchange after 24 h. The volume of obtained solution was reduced on a rotary evaporator and then under a gentle nitrogen stream to obtain a final volume of approximately 0.5 ml. The recovery standard (100 ng deuterated anthracene) was added to each sample before final analysis. A small aliquot (1/10) of the sample was transferred into an insert and PAHs were analysed by GC-MS. The rest of the sample was used for PCB analysis.

The PCB fraction was diluted in 4 ml of hexane and treated with 4 ml of concentrated sulphuric acid by shaking by hand for five minutes. The upper organic layer was then separated and transferred to a Kimax tube. Traces of water were removed by using anhydrous sodium sulphate. Samples were concentrated under a gentle nitrogen stream to obtain a final volume of 20–50 μl. The samples were transferred to an insert and analysed by GC-MS. Before analysis, the recovery standard (14 ng PCB-204) was added to each sample.

Analysis was performed using a Shimadzu GC-MS-QP5000 (Shimadzu, Japan) equipped with an AOC-20i auto injector. Each sample was analyzed for 16 PAHs (EPA) and 28 PCBs. A 1-μl aliquot of a sample was injected in splitless mode (1 min splitless time) at an injector temperature of 280 °C. The GC was fitted with a 30-m ZB-5MS column (0.25 mm i.d., 0.25 μm film thickness). The mass spectrometer interface temperature was set to 280 °C. The oven temperature program for PAHs was as follows: 80 °C for 1 min, 10 °C per min to 250 °C, 7 °C per min to 280 °C, 20 °C per min to 320 °C and held for 10 min. For PCBs: 100 °C for 1 min, 7 °C per min to 250 °C, 4 °C per min to 290 °C and held for 8 min.

QA/QC

Two parallel PSDs were deployed at all sites and duplicate values differed by 10%–30% for each determined concentration. Field and laboratory blanks were analysed in the same manner as deployed samples. The limit of quantification (LOQ) of PAHs ranged between 0.01–0.03 ng l^{-1} for water samples and 0.01–0.04 ng m^{-3} for air samples; for PCBs, the range was 0.05–0.07 ng l^{-1}. All concentrations were corrected by subtracting the value of the appropriate field blank for each sample. Naphthalene concentrations could not be reliably calculated due to their high amounts in the blanks.

The qualification criteria included confirmation of the retention times and *m*/*z* values of the isotope-labelled standards and analytes. The mass fragment with the highest intensity was used for the quantification. Recoveries were routinely monitored using naphthalene-d8, acenaphtene-d10, phenanthrene-d10 and chrysene-d12 for PAHs, and ^{13}C-PCB-52, ^{13}C-PCB-101 and ^{13}C-PCB-138 for PCBs. Recoveries ranged between 81% and 128%, and between 75% and 132% for PAHs in water and air samples, respectively, and between 56% and 98% for PCBs in water.

Data processing

Analytical results were initially calculated as the concentration of target contaminant per PSD. The evaluation of ambient water and air concentrations was then performed using the following equation (Huckins *et al*. 1999):

$$C_A = C_{PSD} V_{PSD} / R_s t \quad (1)$$

where C_A is the ambient concentration of the dissolved contaminant in water or the vaporized contaminant in air, C_{PSD} is the concentration of the contaminant in the sampler, V_{PSD} is the volume of the sampler, R_S is the sampling rate or the volume of water cleared per unit time by a standard 1-g triolein SPMD (membrane + liquid), and t is the exposure time (days). Since both triolein and LDPE have approximately the same specific gravity (0.91), the more easily measurable mass term could be used instead of volume. We assumed that the studied compounds had not reached equilibrium, since their log Kow was > 4 and the exposure time was less than 28 days (Huckins *et al*. 1999). Sampling rates for

PAHs in water were taken from Huckins *et al*. (1999), for PCBs in water from Meadows *et al*. (1999) and for PAHs in air from Cranor *et al*. (2009). Literature data were corrected for the difference in surface area between standard samplers and the samplers used in this study.

Environmental factors such as ambient temperature, biofouling and wind/water flow velocity are known to affect the sampling speed, and sampling rates may therefore vary significantly from site to site (Huckins *et al*. 2002, Bartkow *et al*. 2006). To account for this uncertainty, PCB-30 was used as a performance reference compound (PRC) (Huckins *et al*. 2002). The PRC loss rate constants $K_{e\text{-}PRC}$ (d^{-1}) for each site were determined using the equation:

$$K_{e\text{-}PRC} = \ln(C_{PRC\text{-}0}/C_{PRC})/t \quad (2)$$

where $C_{PRC\text{-}0}$ is the PRC concentration at time 0, C_{PRC} is the PRC concentration at time t, and t is the deployment time (22 days). The calculated loss rate constants for water and summer air samplers were comparable to those determined in earlier calibration studies for compounds with similar partitioning properties. Therefore, we assumed that sampling rates in our study were also similar to earlier-described ones and could be applied for the determination of ambient concentrations in Vesijärvi and the Lahti urban atmosphere. At the same time, a winter sampling campaign was conducted at temperatures significantly lower than those described in the calibration studies and the PRC loss constant could not be reliably determined. The PSD sampling rates are known to increase as a function of temperature (Bartkow *et al*. 2005, Cranor *et al*. 2009); thus, we can suggest that this was also the case in our study. Therefore, we acknowledge that a notable degree of uncertainty is included in the winter PAH concentrations determined in our study.

Statistical analyses

Total concentrations of PAHs and PCBs were calculated as means of two parallel measurements (*see* Appendix 1). Normality of the data was assessed with Shapiro-Wilk's test, as most suitable for small data sets. Since the testing indicated that the data were not normally distributed, dependences between contaminant concentrations and distance from the stormwater outlet were calculated using Spearman's rank-order correlation. Wilcoxon's signed-rank test was used to test the differences in paired data (concentrations of PAHs in the air during different seasons), and a Mann-Whitney *U*-test to analyse independent variables (PAH isomer ratios in Vesijärvi and stormwater drainage). These tests were selected as most appropriate for non-parametric data sets and robust to the low number of samples and outliers. These methods were previously applied by Laureysens *et al*. (2004) and Li *et al*. (2009). Since *Z*-scores could not be reliably calculated for such a small sample, Wilcoxon's *W* and Mann-Whitney's *U* were used for significance determination. All statistical analyses were performed with SPSS (IBM SPSS Statistics 21.0 for Windows, New York, USA).

Results and discussion

PAH and PCB concentrations and distribution in water

The total dissolved concentrations of PAHs in Vesijärvi varied from 1 ng l^{-1} in suburban and rural areas to 3 ng l^{-1} in the vicinity of the urban shore (*see* Appendix 1). The PAH concentrations in lake water were found to be notably higher in urban than in mid- and suburban areas, and they tended to decline significantly with the distance from the urban stormwater outlet (Spearman's rank-order correlation: $r_S = -0.98$, $n = 7$, $p = 0.001$). A similar relation was also found in the Lahti stormwater drainage. The highest total PAH concentration was determined in the urban stormwater well (18 ng l^{-1}) and the lowest in the suburban well (3 ng l^{-1}), while in the mid-urban area the concentration was 8 ng l^{-1} (Fig. 1). The concentrations of PAHs in the Lahti stormwater drainage were 3 to 6 times higher than in the adjacent areas of Vesijärvi.

The total PCB concentrations in Vesijärvi varied from below the limit of quantification (LOQ; *see* Table 1) to 0.4 ng l^{-1}. In the stormwater, the PCB was detected only in the urban location (0.54 ng l^{-1}), while at the mid-urban and

suburban sites it was not present (Fig. 1). Therefore, the concentration of PCBs in the stormwater from the urban location was approximately 1.5 times higher than in the lake samples near the urban shore. The total PCB content of the Vesijärvi water did not show a clear gradient with increasing distance from the urban shore (Spearman's rank-order correlation: $n = 7$, $p = 0.545$). The PCB concentration in the rural control area was < LOQ. This indicates that the Lahti urban area plays a notable role in the contamination of Vesijärvi with PCBs. The lack of significant sources of PCBs in the vicinity of the studied stormwater wells in the mid- and suburban areas might have resulted in low PCB concentrations in these areas. Vesijärvi, however, receives discharge from a number of other stormwater pipelines, some of which may contain notable amounts of PCBs originating from local point sources, e.g. leaching from old buildings and abandoned electrical equipment (Breivik *et al*. 2002, Andersson *et al*. 2004).

PAH and PCB profiles in water

Water samples were analysed for 16 PAHs (EPA), but only eight of them were detected (Table 1). All the quantified compounds contained two to four aromatic rings. Five- and six-ringed PAHs are mostly associated with particulate matter and obviously did not accumulate to detectable concentrations in the PSDs. Amongst individual PAHs, phenanthrene was the most abundant compound in the majority of the samples in the dissolved phase, followed by fluoranthene and pyrene (Fig. 2a–b). In general, individual PAH fingerprints in the samples taken from the Vesijärvi water column did not demonstrate notable changes in relation to the location or distance from the urban shore. The only exception was the rural sampling site, where acenaphthene contributed most significantly to the total dissolved PAHs, followed by phenanthrene (Fig. 2c). This indicates that PAH input sources in urban and rural areas are different and should be considered separately.

The origins of PAHs in the studied samples were also investigated. The main anthropogenic sources of PAHs are combustion processes (pyrogenic) or petroleum leaks (petrogenic). As has previously been described, the origin of PAHs can be determined from the ratio of certain isomers (Gschwend *et al*. 1981, Budzinski *et al*. 1997, Yunker *et al*. 2002). PAHs with molecular masses of 178 and 202 are most often used to distinguish between petroleum and combustion sources. The mass 178 is usually represented by phenanthrene (PHEN) and anthracene (ANT), and the mass 202 by fluoranthene (FLR) and pyrene (PYR). The

Table 1. General information on the chemical compounds determined in our study. LOQ = limit of quantification, ND = not determined.

Compounds	Abbreviations and CAS-numbers	Molecular mass	LOQ		
			in sample (ng)	in water (ng l^{-1})	in air (ng m^{-3})
Acenaphthylene	ACY, 208-96-8	152	0.5	0.02	0.03
Acenaphthene	ACE, 83-32-9	154	0.5	0.01	0.04
Fluorene	FL 86-73-7	166	0.5	0.01	0.04
Phenanthrene	PHEN, 85-01-8	178	1	0.01	0.02
Anthracene	ANT, 120-12-7	178	1	0.01	0.02
Fluoranthene	FLR, 206-44-0	202	1	0.01	0.01
Pyrene	PYR, 129-00-0	202	1	0.01	0.01
Benzo(*a*)anthracene	B(a)A, 56-55-3	228	2	0.03	ND
Chrysene	CHY, 218-01-9	228	2	0.02	ND
Benzo(*b*+*k*)fluoranthene	B(b+k)F, 205-99-2, 207-08-9	252	2	0.03	ND
2,2´,4,5,5´-pentachlorobiphenyl	PCB-101, 37680-73-2	326	0.8	0.05	ND
2,2´,3,4,4´,5´-hexachlorobiphenyl	PCB-138, 35065-28-2	361	0.8	0.07	ND
2,2´,4,4´,5,5´-hexachlorobiphenyl	PCB-153, 35065-27-1	361	0.8	0.09	ND

isomer ratios PHEN/ANT > 10 have been found to be characteristic of petrogenic inputs, while PHEN/ANT < 10 indicates the predominance of pyrogenic impacts, although borderline values are not so precise and PHEN/ANT < 15 is usually also related to combustion. At the same time, the ratios FLR/PYR > 1 have been reported to relate to a pyrogenic and FLR/PYR < 1 to a petrogenic origin (Sicre *et al*. 1987, Wise *et al*. 1988, Benner *et al*. 1989). The reliability of this source appointment method is challenged by numerous uncertainties (Galarneau 2008, Ravindra *et al*. 2008, Dvorska *et al*. 2011). Individual sources of PAHs are themselves often subject to variation, while PAH ratios at sites distant from sources may be altered due to environmental chemical reactions (Esteve *et al*. 2006, Perraudine *et al*. 2007, Kim *et al*. 2009). However, the applicability of the diagnostic PAH ratio was found to be satisfactory for samples taken within a short distance from a distinctive source (Dvorska *et al*. 2011). In our study, the majority of the sampling sites were situated within 1 km from the urban area. Asphalt leaching, traffic emissions and domestic heating during the cold season are the main distinctive sources to which urban-derived PAH contamination is often attributed. Therefore, we can expect PAH diagnostic ratios to be applicable for reliable source appointment in this case.

The FLR/PYR ratio was lower in the samples from the stormwater than from Vesijärvi. The PHEN/ANT ratio was higher in the lake than in the stormwater (Fig. 3a). The difference between the isomer ratios in stormwater (n = 3) and the Vesijärvi water (n = 8) was significant (Mann-Whitney U-test (U = 2, p = 0.025 for both ratios). The lake sample from the vicinity of the urban shore (Fig. 3a, sample 3 in Appendix 1) exhibited an exceptionally low FLR/PYR ratio (0.7), presumably due to the effect of stormwater discharge. This suggests that petrogenic sources (leaching from asphalt) contribute significantly to the contamination of Lahti stormwater with PAHs and also affect the water quality of Vesijärvi in the immediate vicinity of the urban shore. However, in the samples taken further away from the urban shore, source-defining ratios were higher and more similar to each other, indicating a predominance of pyrogenic PAHs, transported by other means

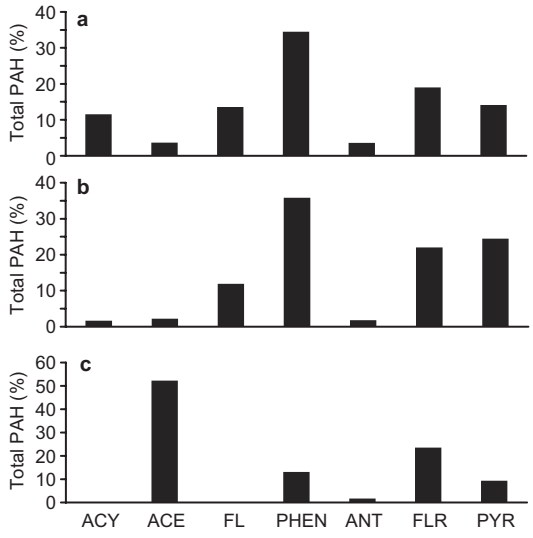

Fig. 2. Contributions of polycyclic aromatic hydrocarbons (PAHs) in water samples from (**a**) Vesijärvi, (**b**) Lahti urban stormwater, and (**c**) Vesijärvi rural site. ACY = acenaphtylene, ACE = acenaphtene, FL = fluoranthene, PHEN = phenanthrene, ANT = anthracene, FLR = fluoranthene, and PYR = pyrene.

that urban runoff, presumably atmospheric transport. PAH concentrations also rapidly declined within 500 m from the shore (Fig. 1). Similar was previously found for the Vesijärvi sediments (Honkonen and Rantalainen 2013).

Water samples were analysed for 28 PCBs, but only three congeners were detected (Table 1). PCB-153 was the most abundant in all of the samples, followed by PCB-138 and PCB-101 (Fig. 5). This pattern is comparable with the fingerprint of commercial mixtures of Aroclor fingerprint (Aroclor 1242, 1254 and 1260), which were used, for instance, in paint manufacturing. Similar profiles were obtained in our previous studies of sediments from Vesijärvi and urban stormwater traps in Lahti (Honkonen and Rantalainen 2013), as well as for urban runoff in Switzerland (Rossi *et al*. 2004), for the Alna river in Oslo (Allan *et al*. 2011) and for Dungeness crabs from the west coast of the British Columbia (Ikonomou *et al*. 2002).

PAH distribution and profiles in the air

The total atmospheric concentrations of gase-

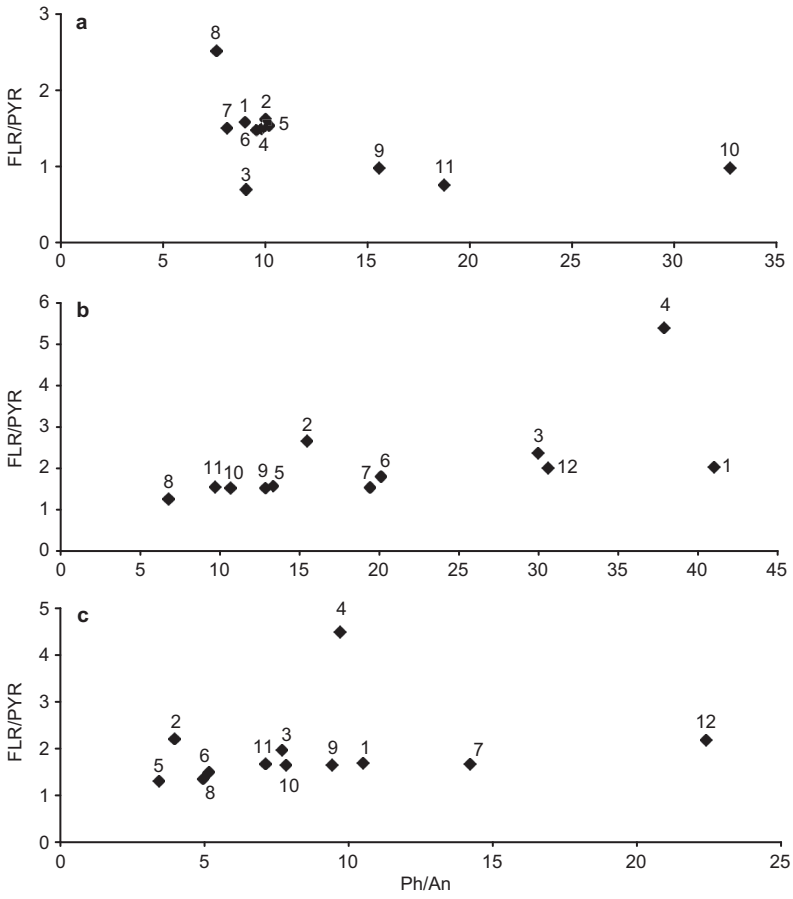

Fig. 3. Source-defining ratios of PAHs in (**a**) water samples from Vesijärvi (1–8) and Lahti stormwater drainage (9–11), (**b**) air samples taken during the non-heating (1–6) and heating (7–12) seasons, and (**c**) air samples taken during the non-heating and heating seasons estimated for particulate phase.

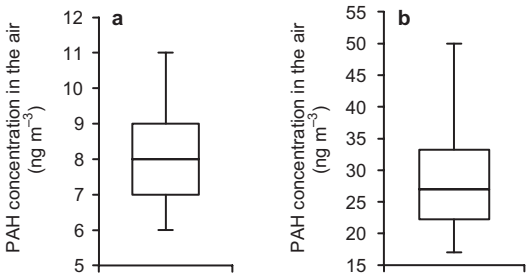

Fig. 4. Total atmospheric PAH concentrations in (**a**) summer, and (**b**) winter. The line inside the box is the median, the bottom and top of the box are first and third quartiles, the whiskers indicate maximum and minimum values.

ous PAHs in the air varied from 6 ng m^{-3} to 11 ng m^{-3} in the summer, and between 17 and 50 ng m^{-3} in the autumn (Fig. 4), and the difference between seasons was significant (Wilcoxon's signed-rank test: $W = 21$ $n = 6$, $p = 0.025$). It has recently been shown that in moderate climates, large cities with a high traffic intensity, a high impervious surface coverage and heating systems producing low PAH emissions (e.g. natural gas), temperature-dependent processes such as condensation and volatilization from impervious surfaces play a large role in controlling the distribution of PAHs and can result in elevated summer air concentrations (Gustafsson and Dickhut 1997, Melymuk *et al*. 2012). However, in less urbanized areas with a lower traffic intensity and impervious surface coverage, and possibly greater use of oil, coal or wood heating (Gingrich and Macfarlane 2002, Dvorska *et al*. 2011), emissions from fossil fuel combustion such as domestic heating contribute more to PAH concentrations in air, leading to higher winter concentrations (Liu *et al*. 2006, Ma *et al*. 2010, Melymuk *et al*. 2012). In addition, photodegradation may significantly lower PAH con-

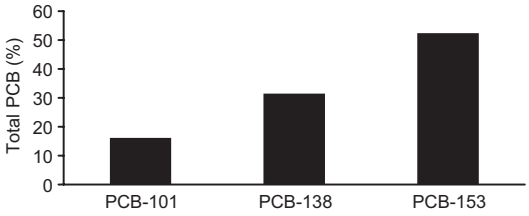

Fig. 5. Contributions of PCBs in water samples from Vesijärvi and Lahti urban stormwater.

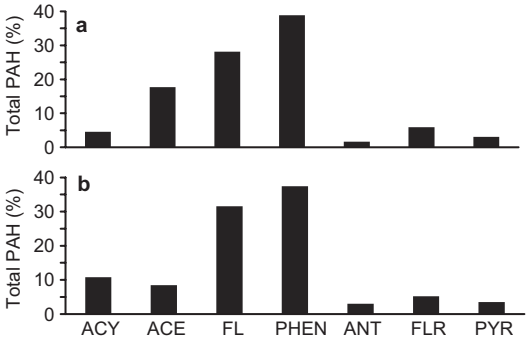

Fig. 6. Contributions of PAHs in air sampled from the Lahti urban area during (**a**) non-heating, and (**b**) heating seasons. For symbol explanations *see* Fig. 2.

centrations in summer, especially if the number of rings is < 4 (Melymuk *et al*. 2012).

In our study, concentrations of PAHs in the ambient air were significantly lower in the summer than in the autumn. The heating system in the Lahti urban area is mostly based on oil, coal and wood combustion, while the traffic intensity and impervious surface coverage is moderate. Therefore, PAH emissions increase in the cold season due to the enhancement of heating combustion processes. Even though autumn air sampling rates could not be calibrated according to the PRC loss in our study, possible changes would most likely increase the calculated concentrations, making the difference even more pronounced. Interestingly, the total amounts of contaminants at the suburban site was amongst the highest in both of the seasons. The same result was also obtained for the stormwater trap sediment in our previous study (Honkonen and Rantalainen 2013). This suggest unknown local source, affecting both air and sediment quality. PCBs were not detected in the air samples.

Phenanthrene was the most abundant individual PAH in all air samples, followed by fluorene and acenaphthene during the non-heating period (from May to September), and by fluorene and acenaphtylene during the heating season (Fig. 6). Source-defining PAH ratios PHEN/ANT and FLR/PYR were also calculated for the air samples. Interestingly, in multiple cases they suggested a petrogenic origin (PHEN/ANT > 10), which is not typical for atmospheric PAHs (Fig. 3b). However, the source-defining ratios were originally developed for solid matter, and the difference between phenanthrene and anthracene in gas–particle partitioning coefficients could explain this shift. In previous studies, water–particle partitioning was found to be similar for anthracene-phenanthrene and fluoranthene-pyrene (Ko and Baker 1994, Fernandez *et al*. 1997, Gustafson and Dickhut 1997, Luo *et al*. 2008). However, the tendency was rather different for the air–particle partitioning case (*see* Appendix 2). In the air samples taken during the heating season (samples 7–12 in Appendix 1), the average percentage in the gaseous phase was 21% (PHEN) *vs*. 27% (ANT), and the difference was even greater in the non-heating season (samples 1–6 in Appendix 1, 3% *vs*. 12%), which obviously leads to changes in the PAH ratios. In the other cases, the partitioning behaviour of the source-defining compounds was similar and did not significantly affect the results. If concentrations are corrected according their partitioning onto particles, the PHEN/ANT ratio in the majority of samples is less than 10 and therefore indicates pyrogenic sources (Fig. 3c).

Evaluation of potential impact on the boreal Vesijärvi ecosystem

The calculated concentrations of PAHs and PCBs were compared with international guidelines suggested in a compilation by US EPA (2009). This compilation contains information on the US, Canadian and European threshold values. Dissolved concentrations of individual PAHs and PCBs in the water column of Vesijärvi were lower than the international guideline values. However, sediment concentrations were earlier found to be elevated near the urban shore and exceeded environmental threshold values in

many cases (Honkonen and Rantalainen 2013). This suggests that the contamination load produced by the Lahti urban area poses notable risks to the adjacent lake ecosystem. Guidelines for PAH concentrations in the ambient air are usually related to the amount of benzo(*a*)pyrene, which was not detected in our study, and a comparison could not therefore be conducted.

Contaminant concentrations in the Vesijärvi water column were also compared with the findings of similar previous studies. Concentrations of PAHs were one to two orders of magnitude lower than in several Chinese rivers, in the Elizabeth River, Chesapeake Bay and New York Harbour in the US, and in the Mulde River in Germany, located in the vicinity of highly urbanized and industrialized areas. Moderately-urbanized and non-industrial areas of Raritan Bay in the US, Lake Maggiore in Italy, the northwestern Black Sea and adjacent estuaries contained PAHs at similar levels to those in Vesijärvi. However, the dissolved PAHs determined in our study were slightly more abundant (by less than one order of magnitude) than in remote mountain lakes of Norway, Spain and Italy (Table 2). It should also be taken into account that Vesijärvi sediments from the vicinity of the Lahti urban shore were earlier found to be contaminated with PAHs and PCBs, which exceeded environmental guidelines by up to 2.5-fold (Honkonen and Rantalainen 2013). Although the PAH concentrations in Vesijärvi were comparable to those reported in previous studies, the PAH concentrations in the stormwater were several orders of magnitude lower than most of the earlier-measured values (Table 2). To our knowledge, the only previous study investigating PAH concentrations in a stormwater drainage system using SPMDs was conducted by Komarova *et al*. (2006). The results of that study were very similar to the findings from Lahti urban drainage. However, all the other examples available for comparison used automatic meters. These provide more accurate results, especially during high-flow events, which SPMDs might not be able to register due to their limited uptake rates. Furthermore, the studies conducted by Wium-Andersen *et al*. *(*2009) and Vollertsen *et al*. (2009) lasted for over a year. It is known that heavy rainfall and snowmelt in northern areas are amongst the most polluting events for urban stormwater. Since our experiment was conducted during one month in the summer, it could not take into account such seasonal changes in stormwater quality as in the above-mentioned studies. In the USA, the levels of stormwater contamination with PAHs are often found to be significantly higher than in the Nordic countries, due to the higher population, more intensive traffic and widely used coal-tar sealcoats for pavements (Vanmetre *et al*. 2008, Watts *et al*. 2010). The concentrations of PCBs in the water column of Vesijärvi were similar to those in the Alna river in Oslo (Allan *et al*. 2011), and up to one order of magnitude higher than determined by Sobek *et al*. (2004) in the Baltic Sea off the Swedish coast (Table 2).

Atmospheric PAH concentrations in the Lahti urban area during both heating and non-heating seasons were lower than in large industrialized cities and their immediate surroundings in China, the US and UK, but similar to the values found in moderately urbanized and rural locations in previous studies (Table 3).

Conclusions

The results of this study strongly suggest that the Lahti urban area produces a notable load of organic pollutants to the adjacent atmosphere and Vesijärvi. Stormwater discharges containing PCBs and petrogenic PAHs appeared to mainly affect the immediate vicinity of the outlets, while majority of the urban-derived pyrogenic PAHs are transported out of the city, predominantly by atmospheric transport. Atmospheric PAHs are rather evenly distributed over the urban area and surroundings of Lahti, followed by partial deposition into Vesijärvi. However, urban-derived contamination was not found to reach the rural areas, where the origins of PAHs appeared to be different. ANT increase in the input of pyrogenic PAHs to the atmosphere in the Lahti urban area, attributed to the enhancement of combustion processes (e.g. heating, vehicle engine emissions), was detected in the cold season. Comparison with environmental guideline values shows that the Lahti urban area contributes significantly to the contamination of Vesijärvi with hydrophobic organic pollutants and may pose notable

Table 2. Total concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in Vesijärvi and Lahti stormwater drainage, compared to those reported in earlier studies. HV = high-volume sampling; PS = passive sampling.

Location	Compound class, concentration range, ng l^{-1} (type of waterbody)	Sampling method	Reference
Chesapeake Bay, USA	PAH, 20–25 (natural)	PS	Gustafson and Dickhut 1996
Elizabeth River, USA	PAH, 66 (natural)	PS	Gustafson and Dickhut 1996
Mulde, Germany	PAH, 10–185 (natural)	PS	Vrana *et al.* 2001
New York Harbour	PAH, 31–44 (natural)	HV	Gigliotti *et al.* 2002
Raritan Bay, USA	PAH, 3–7 (natural)	HV	Gigliotti *et al.* 2002
Remote mountain lakes	PAH, 0.3–0.6 (natural)	HV	Vilanova *et al.* 2001
Lake Maggiore, Italy	PAH, 2.9 (natural)	HV	Olivella 2006
Vesijärvi, Finland	PAH, 0.8–2.8 (natural)	PS	this study
Baltic Sea, Swedish coast	PCB, 0.004–0.04 (natural)	HV	Sobek *et al.* 2004
River Alna, individual	PCB, 0.001–0.08 (natural)	PS	Allan *et al.* 2011
Vesijärvi, Finland	PCB, < LOQ–0.4 (natural)	PS	This study
Massachusets, USA	PAH, 300–5800 (stormwater)	HV	Menzie *et al.* 2002
Odense, Denmark	PAH, 250 (stormwater)	HV	Wium-Andersen *et al.* 2011
Aarhus, Denmark	PAH, 350 (stormwater)	HV	Wium-Andersen *et al.* 2011
Brisbane, Australia	PAH, 19 (stormwater)	PS	Komarova *et al.* 2006
Lahti, Finland	PAH, 3–18 (stormwater)	PS	this study
Switzerland	PCB, < LOQ–400 (stormwater)	HV	Rossi *et al.* 2004
Lahti, Finland	PCB, 0.54 (stormwater)	PS	this study

Table 3. Polycyclic aromatic hydrocarbons (PAHs) concentrations (ng m^{-3}) in the air. HV = high-volume sampling, PS = passive sampling.

Location	Concentration (ng m^{-3})		Sampling method	Reference
	heating season	non-heating season		
Birmingham, UK	130	23	HV	Harrison *et al.* 1996
Harbin, China	83	26	HV	Ma *et al.* 2010
Chicago	120–190	72	HV	Simcik *et al.* 1998
Lake Michigan	NA	8–40	HV	Simcik *et al.* 1998
UK, rural*	2–10	2–10	PS	Gioia *et al.* 2006
Norway, rural*	< 0.1–20	< 0.1–20	PS	Gioia *et al.* 2006
Pearl River, China	NA	5–50	PS	Liu *et al.* 2006
Springwood, Australia	NA	4	PS	Bartkow *et al.* 2004
Lahti, Finland	16–50	5–10	PS	this study

* Sampling conducted for over a year, no differentiation between heating and non-heating seasons.

risks to the aquatic ecosystem. Therefore, regular updates are needed to monitor temporal changes in the urban-derived contamination and prevent possible increases in the pollutant load and toxicological risks they may bring.

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Appendix 1. Total polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in water (ng l^{-1}, samples 1–11), total PAHs in air (ng m^{-3}) during non-heating season (samples 12–17) and heating season (samples 18–23).

Sample number	Distance from outlet (m) or site type	Parallel 1	Parallel 2	Average
1	700	1.05	1.32	1.19
2	500	1.61	2.13	1.87
3	100	2.22	1.96	2.09
4	500	1.49	1.27	1.38
5	1000	0.55	0.88	0.71
6	1000	0.97	0.63	0.80
7	1500	0.53	0.75	0.64
8	8000	0.63	1.04	0.83
9	stormwater suburban	2.17	2.93	2.55
10	stormwater midurban	5.85	5.54	5.70
11	stormwater urban	12.88	13.61	13.24
12	mid-urban	5.99	7.35	6.67
13	urban	10.01	11.91	10.96
14	urban	5.96	8.29	7.13
15	urban	9.17	7.84	8.51
16	suburban	9.90	7.87	8.89
17	rural	5.09	6.10	5.59
18	mid-urban	16.81	22.98	19.89
19	urban	44.87	51.30	48.08
20	urban	22.62	27.80	25.21
21	urban	31.01	36.66	33.83
22	suburban	27.81	26.04	26.93
23	rural	14.55	17.80	16.18
1 (PCB)	700	ND	ND	ND
2 (PCB)	500	2.45	3.83	3.14
3 (PCB)	100	3.72	5.66	4.69
4 (PCB)	500	2.99	6.01	4.50
5 (PCB)	1000	3.56	6.52	5.04
6 (PCB)	1000	0.61	3.18	1.90
7 (PCB)	1500	1.88	3.58	2.73
8 (PCB)	8000	ND	ND	ND
9 (PCB)	Stormwater suburban	ND	ND	ND
10 (PCB)	Stormwater mid-urban	ND	ND	ND
11 (PCB)	Stormwater urban	1.56	2.80	2.18

Appendix 2. Polycyclic aromatic hydrocarbons (PAHs) partitioning between dissolved and particulate phases. For the purpose of this work, percentages of individual PAHs in the particulate phase of water and air were calculated based on Harrison *et al.* (1996), Fernandez *et al.* (1997), Gustafson and Dickhut (1997), Simcik *et al.* (1999), Ko and Baker (2004), Shimmo *et al.* (2004), Sobek *et al.* (2004), Luo *et al.* (2008) and Ma *et al.* (2010).

Compound	PAHs (%)		
	in water	in air, non-heating season	in air, heating season
Phenanthrene	42	3	21
Anthracene	40	12	27
Fluoranthene	56	15	55
Pyrene	56	17	53